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# KINETIC SPECIFICS OF THE SYNTHESIS OF LUMINESCENT MATERIALS USING THE SOL-GEL METHOD

N. V. Popovich<sup>1</sup> and V. V. Fedorov<sup>1</sup>

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Based on the sol-gel method for producing luminescent silicate materials, the process kinetics is studied for the initial stages of hydrolysis and polycondensation of tetraethoxysiloxane for different temperatures and component ratios. A model of the process is proposed, and reaction rate constants are determined. A conclusion is made on the limiting effect of the polycondensation stage up to the moment of gel formation.

Various countries have recently carried out intensive research in developing the principles of the sol-gel process, which is a new method for production of silicate materials. Compared to the traditional technologies, this method has several advantages: better purity and homogeneity of the products, the possibility of controlling the structure of the material at all stages of the process. By varying the conditions of synthesis, it is possible to obtain amorphous and crystalline materials in the form of solid samples, films, fibers, and powders [1]. Several papers published in recent years discuss this subject [2–4].

The present paper continues a series of studies in the field of sol-gel synthesis of silicate luminescent materials [5–7]. It has been shown that the structure and properties of the final products are primarily determined by the conditions of preparation of the initial solutions and gel formation. At the same time, the mechanism of the sol → gel transition and the chemical processes and structural transformations that occur here are among most complicated and least investigated subjects.

The purpose of the present work is to substantiate a simple kinetic model of the initial stage of the process (up to the moment of gel formation) that would make it possible to adequately analyze existing experimental data.

The most accessible parameter found as a function of time is the kinematic viscosity of the system. However, it cannot be related uniquely to the concentration of the initial monomer tetraethoxysilane (TEOS) or the inorganic polymer  $Q$ . To describe the kinetics of the process versus the change in the viscosity, the following assumptions were made:

– the system viscosity increases due to the increasing concentration of the product  $Q$ , and the Schtaudinger equation is satisfied at the same time [8]:

$$\eta_{sp} = KM_c, \quad (1)$$

where  $\eta_{sp} = (\eta - \eta_0)/\eta_0$  ( $\eta$  is the measured viscosity, Pa · sec;  $\eta_0$  is the initial viscosity of the system);  $K$  is a constant that is characteristic of the given homological polymer series in the given solvent;  $M$  is the molar weight of the polymer at the concentration  $c$ , mole/dm<sup>3</sup>;

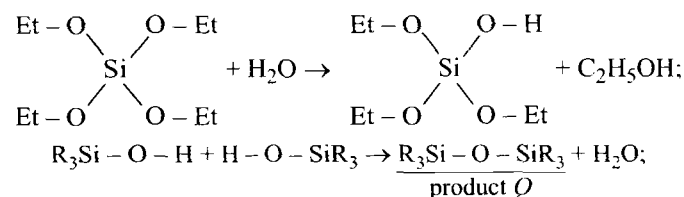
– in the initial stage the sol-gel process proceeds as a sequential reaction of hydrolysis and polycondensation, where both steps obey formal kinetics of the first order.

The following arguments can be put forward to substantiate the above assumptions.

First, the Schtaudinger equation was obtained based on the Einstein model, implying scarcely deformed “rigid” polymolecular formations (“rods”), which usually do not agree well with real organic polymers, having a very flexible –C–C– chain. However, the Schtaudinger assumptions are quite correct for inorganic silicate polymers due to the scarcely labile –Si–O–Si– structure.

Second, hydrolysis and polycondensation processes can obviously proceed both successively and simultaneously. However, according to the data in [9], the hydrolysis rate constant exceeds by more than two orders of magnitude the polycondensation rate constant, i.e., in a first approximation the process can be regarded as a sequential reaction. Hydrolysis of TEOS in the presence of an excess of water is a first-order reaction. The stage of polycondensation up to the moment of gel formation can be represented as the reaction of a relatively small quantity of growing polymer molecules  $(R)_n$ –SiOH with the excess hydroxyl groups of the monomer and can be described by a first-order kinetic equation.

The above assumptions made it possible to take as a basis the following model of the process, which includes hydrolysis and polycondensation stages [10]:



<sup>1</sup> D. I. Mendeleev Russian Chemical Engineering University, Moscow, Russia.

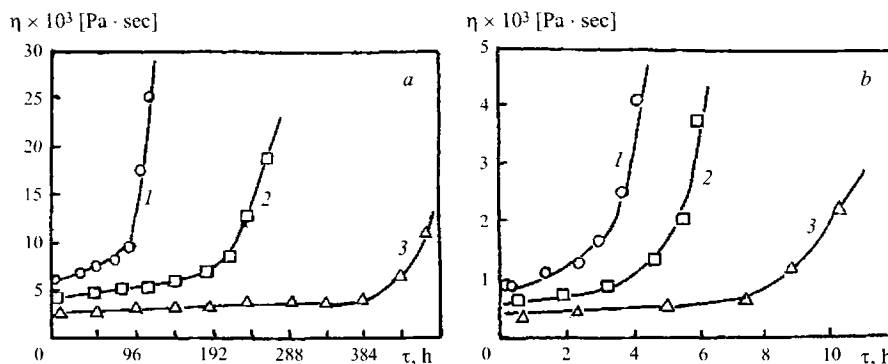
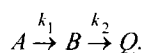


Fig. 1. Change in the solution viscosity in time for different ratios  $H_2O : TEOS$  ( $R$ ) and the temperatures 293 K (a) and 353 K (b): 1, 2, and 3)  $R = 15, 30$ , and 60, respectively.

or formally



For  $k_1 \gg k_2$ , the following expression can be obtained:

$$[Q] = a(-e^{-k_2\tau}),$$

where  $a$  is the initial concentration of the monomer, mole/dm<sup>3</sup>;  $k = k_2$  is the reaction rate constant, sec<sup>-1</sup>;  $\tau$  is the time, sec.

By substitution of  $c$  for the concentration  $[Q]$  we will get

$$\ln c = \ln a + k\tau.$$

On the other hand, it follows from Eq. (1) that

$$\ln c = \ln \eta_{sp} - \ln (KM).$$

And finally

$$\ln \eta_{sp} = \ln (KMa) + k\tau.$$

If

$$\ln (KMa) = \alpha,$$

then

$$\ln \eta_{sp} = \alpha + k\tau. \quad (2)$$

Equation (2) provides the possibility of calculating the kinetic parameters of the initial stage of the sol-gel process.

The binary system  $ZnO - SiO_2$  was selected for experimental verification of the above assumptions. The initial

components were TEOS, zinc nitrate, an aqueous alcohol solution  $H_2O + C_2H_5OH$ , and the hydrolysis catalyst  $HNO_3$ . The solution preparation method was described earlier in detail [5]. For the purpose of studying the effect of the component ratio on the rate of the gel formation process, the molar ratio  $H_2O : TEOS$  ( $R$ ) was varied in the range of  $R = 15 - 60$ . The viscosity of the solutions was determined with an Ostwald capillary viscosimeter.

Figure 1 shows the change in the viscosity of solutions having different ratios  $H_2O : TEOS$  and different thermostat-control temperatures.

An analysis of the kinetic data obtained made it possible to determine the process rate constants for different ratios  $H_2O : TEOS$  and the parameters of the Arrhenius equation for the temperature dependence (Tables 1 and 2). Table 2 also contains values of the steric factor  $p$  estimated in the framework of the theory of active molecular collisions by comparing the collision factor  $z_0$  with the pre-exponential factor  $A$  in the Arrhenius equation:

$$p = A/z_0,$$

where  $A = ke^{E/RT}$ .

The calculated value  $z_0 \approx 3 \times 10^{13} \text{ sec}^{-1}$  scarcely depends on the temperature.

It can be seen from Table 1 that the process rate constant is rather small, namely, of the order of  $10^{-6} - 10^{-4} \text{ sec}^{-1}$ , which agrees well with data of other authors [9] who studied polycondensation processes. The rate constant of hydrolysis of the initial alkoxy silane is significantly larger, which suggests that the rate of transformation (up to the moment of gel formation) is limited on the whole by the stage of polycondensation. It should be noted that the process rate constant virtually does not depend on the component ratio ( $R = 15 - 60$ ). This can be accounted for by the fact that within the investigated interval, the condition of sufficient excess of the monomer with respect to the growing polymer fragments is always satisfied, i.e., the pseudomonomolecular process of polycondensation does not change.

TABLE 1

$T, K$	$R = 15$	$R = 30$	$R = 60$
293	$(8.88 \pm 0.50) \times 10^{-6}$	$(3.53 \pm 0.38) \times 10^{-6}$	$(5.61 \pm 0.54) \times 10^{-6}$
313	$(3.08 \pm 0.45) \times 10^{-5}$	$(3.93 \pm 0.36) \times 10^{-5}$	$(1.20 \pm 0.58) \times 10^{-5}$
333	$(2.47 \pm 0.31) \times 10^{-4}$	$(6.47 \pm 0.73) \times 10^{-5}$	$(5.33 \pm 0.13) \times 10^{-5}$
353	$(2.64 \pm 0.14) \times 10^{-4}$	$(2.88 \pm 0.11) \times 10^{-4}$	$(1.70 \pm 1.14) \times 10^{-4}$

TABLE 2

Kinetic parameters	H <sub>2</sub> O : TEOS		
	R = 15	R = 30	R = 60
$E$ , kJ/mole	$49.9 \pm 0.7$	$57.9 \pm 0.8$	$65.4 \pm 2.1$
$A$ , sec <sup>-1</sup>	$7.0 \times 10^4$	$7.4 \times 10^5$	$8.2 \times 10^6$
$p$	$2 \times 10^{-10}$	$2 \times 10^{-9}$	$3 \times 10^{-8}$

At the same time, a certain increase in the activation energy is recorded (see Table 2) as the water content in the system increases. R. Eiler [11] quotes in his monograph data of various authors on the effect of the pH of the solution on the activation energy of the stage of polycondensation  $E$ . It is noted that  $E = 65.1$  kJ/mole for pH = 5.5 and  $E = 40.3$  kJ/mole for pH = 8.5. The authors of [12, 13] believe that this is related to certain changes in the mechanism of protolytic catalysis. The present investigation was able to establish a similar effect of the pH on the process activation barrier; however, this was due not to pH variations related to a varying acid content in the system (this value remained constant), but to the fact that the reaction took place in an aqueous-organic medium. As the relative content of H<sub>2</sub>O increases ( $R = 15 \rightarrow 60$ ), the pH decreases, since  $\text{pH} = -\lg a(\text{H}^+)$ , and the higher the water content in the medium, the higher the degree of dissociation of the catalyst acid, which is a strong electrolyte. Thus, the ratio of the reactants, besides directly affecting the process kinetics, also has an indirect effect through the change in the pH of the medium.

It is of interest that the pre-exponential factor  $A$  and, accordingly, the steric factor  $p$  increase as the relative content of water increases. On the one hand, some of this increase can be attributed to the threefold increase in the error of estimation of  $E$  in going from  $R = 15$  to  $R = 60$ . However, this effect is due mainly to the fact that in more water-diluted solutions, a growing polymer molecule encounters fewer spatial obstacles in reaching a reaction center. It is noteworthy that the value of  $p$  is extremely low and is typical of so-called "anomalously slow" reactions of the type of Menshutkin reactions. On the whole, one can speak of substantial spatial obstacles in the stage of polycondensation and low specific rates of the process.

The correlation of the kinetic data in the present study with the data in [14], in which the Arrhenius equation parameters are indicated for gel formation in a calcium-bearing system with a molar ratio  $R = 6$ , is noteworthy. The reaction rate constant calculated by us based on these data for a tem-

perature of 20°C was  $2 \times 10^{-6} \text{ sec}^{-1}$ , which agrees well with the values in Table 1 for  $R = 15$  and  $T = 293$  K. Since the author of [14], as distinct from the present study, based his kinetic estimates not on viscosity measurement but on the gel formation duration, such agreement between the data can be regarded as further evidence of the correctness of the model we suggested.

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